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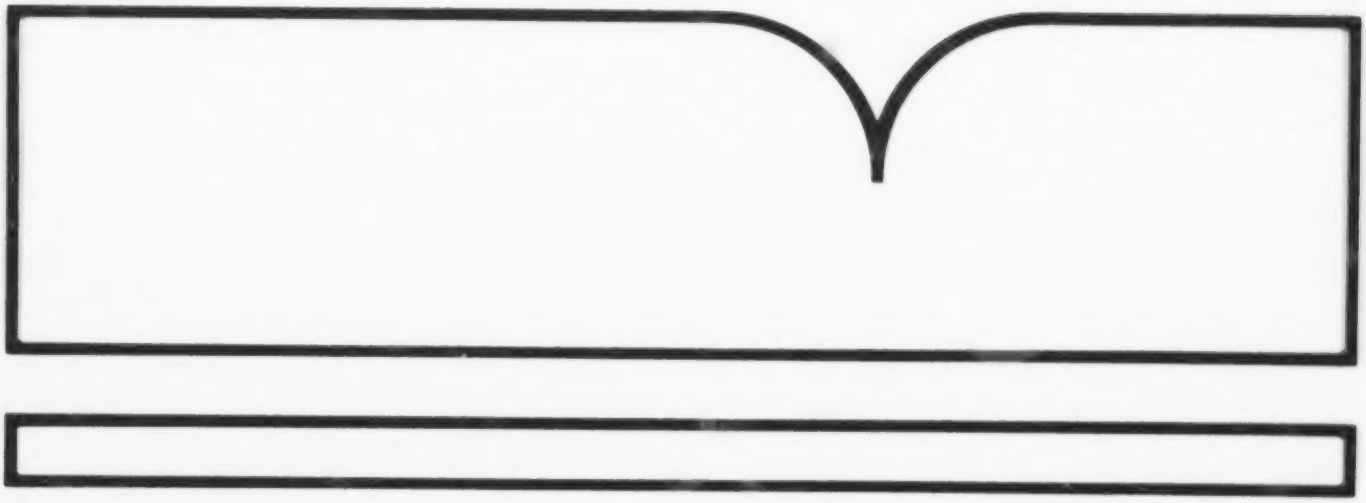

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16. ABSTRACT

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Receptor Modeling Study of Denver Winter Haze

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JOURNAL ARTICLE

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■ A multiple-regression single-element tracer method in combination with SO_2 and NO_x emissions inventory scaling was used to estimate source contributions to fine and coarse aerosol mass and light extinction, measured in Denver during January 1982. Motor vehicles were the largest contributor to average fine particle mass (42%) and daytime light extinction (47%). Electric power generation was next largest, at 23% and 44%, respectively. Wood burning contributed 12% and 14%, respectively. The electric power contribution estimate was based entirely on emission inventory scaling and thus correspondingly more uncertain. Fine mass concentrations averaged only half as large as those measured in a similar field study conducted in late 1978. During high-pollution periods, the motor vehicle impact during the day and the woodsmoke impact during the night were relatively greater than their averages. Other notable differences from the 1978 results included a reduced value for b_{ap}/b_{sp} (0.24), a reduced value for the ratio of elemental carbon to fine particle carbon (0.23), and an absence of non-sulfate sulfur in the fine mass fraction. The differences are in the direction of lessening the distinctiveness of Denver relative to other U.S. airsheds.

Introduction

During wintertime, Denver frequently experiences periods of highly visible haze ("Denver Brown Cloud"), made all the more noticeable by the scenic setting of the city. The most comprehensive field study of the origins of Denver's winter haze occurred in November–December 1978 (*1–6*). While prior studies (*7–9*) had emphasized the haze origins in terms of meteorological and topological factors, the 1978 study focused on measurements of aerosol and gas chemical composition, which were then combined with receptor model concepts to apportion the atmospheric aerosol, gases, and visibility reduction (extinction) to emission sources. The 1978 study results thus offered the possibility for haze-control decision making that was lacking before then.

Examination of the 1978 results reveal several unusual findings: a remarkably high value (45%) for the average ratio of absorption to scattering by atmospheric particles (*4*); an unusually high value (46%) for the average amount of elemental carbon (black soot) relative to total carbon in the fine particle fraction (*1*), with a correspondingly high contribution (38%) made by elemental carbon to total extinction (*4*); 44% of the fine particle sulfur in a non-sulfate, but otherwise unknown, form (*1*). Such characteristics, if true, would underline the distinctive nature of the Denver area relative to other U.S. airsheds. Additionally, since the receptor modeling was based on emissions inventory scaling of the major aerosol chemical species (sulfate, volatilizable and elemental carbon, and nitrate), concern over the measurement of any of these species translates into a concern over the resulting source apportionment.

A follow-up receptor modeling field study, sponsored by the U.S. EPA, was performed in January 1982. Beyond an interest in reexamining the measurement issues listed above, the study provided the opportunity for additional activities: particulate nitrate measurement with best available technology; investigation of the human perception of visual air quality relative to instrumental surrogates; use of a multivariate receptor model for mass and extinction source apportionment less dependent on (frequently inaccurate) emissions inventories than the 1978 procedure.

Previous articles resulting from the 1982 study have reported on the particle absorption to scattering ratio (*10*) and on human judgments vs. instrumental measures of visual air quality (*11*). This article addresses the remaining results from the 1982 study, superseding earlier preliminary accounts (*12, 13*). Most of the comparisons presented here reference the results produced by General Motors Research Laboratory (GMR) in the 1978 study. This is because the EPA and GMR results should be the more comparable, as the same sampling site was used.

Source apportionment of measured aerosol concentrations was performed by combining the multiple linear regression receptor model approach of Kleinman et al. (*14*), with SO_2 and NO_x emissions inventory scaling. The former accomplished the apportionment of primary aerosol emissions, while the latter was necessary for the apportionment of the secondary sulfate and nitrate mass contributions. As will be seen, less than half the measured mass is apportioned in the relatively crude emissions inventory scaling step, resulting in at least a theoretical improvement of the source apportionment accuracy over that of the 1978 procedure, which was wholly dependent on inventory scaling. The source apportionment of extinction was subsequently accomplished through the use of "generalized" source profiles developed in the course of the mass apportionment step.

Thurston and Spengler (*15*) have proposed a generalization of the Kleinman procedure that combines multiple linear regression with a *quantitative*, rather than diagnostic, use of factor analysis in the first step of the procedure. Because of some unsatisfactory features (described later) of the factor analysis of the present data set and recent strong criticisms (*16*) of factor analysis as a quantitative receptor modeling tool, we chose not to implement the new procedure in this study. Our analysis makes minimal use of factor analysis and depends on an "all possible subsets regression" algorithm to establish the regression predictors.

The Experiment

Site Descriptions. The field measurements were performed over the 20-day period January 11–30, 1982. Most of the measurements were performed in the large paved parking lot of the Denver Mile High Kennel Club (MHKC), located 10 km northeast of Denver's city center in an area of low residential density and light industry.

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The MHKC facility was not otherwise in use during the study. For comparison purposes, the roof (100 m above street level) of the Cadillac Fairview Building (CFB), located close to the city center of Denver, was also used as a sampling site.

Aerosol Sampling. Aerosol instrumentation at the MHKC was as follows: A 16.7 L min^{-1} Beckman dichotomous sampler using 2-μm pore size Teflon filters was operated on a 12-h schedule (0600–1800 and 1800–0600 MST) to collect simultaneously fine (0–2.5 μm) and coarse (2.5–15 μm) aerosol samples suitable for X-ray fluorescence and ion chromatographic analysis (cut points in terms of aerodynamic diameter throughout report).

A prototype diffusion denuder sampler (DDS), similar to that described by Shaw et al. (*17*), was used to perform simultaneous measurements of particulate nitrate and gaseous nitric acid through collection on nylon filters (Millipore 1-μm pore size). The sampled nitrate was restricted to the fine fraction, as defined by a stainless steel cyclone on the inlet whose cut point was 2.5 μm at the sampler's 3 L min^{-1} flow rate. The sampler operated on the same 12-h schedule as the dichotomous sampler.

A prototype 50 L min^{-1} sampler was used to collect "fine" aerosol samples on quartz (Pallflex type 2500 QAST) for aerosol carbon analysis, on a 4-h schedule (0600–1000, etc.). After the study, it was discovered that the cyclone, which was expected to reject particles larger than 2.5-μm diameter, had been assembled incorrectly, resulting in an estimated cut point of 7 ± 2 μm. The probable effect of this on the measured carbon concentrations is discussed below.

At the CFB site, a Beckman dichotomous sampler only was operated. Flow rate settings and measurements of all samplers were performed with a dry test meter. The measurement frequency was twice per day for the DDS, once per day for the carbon sampler, and at the beginning, middle, and end of the study for the dichotomous samplers (the latter instruments were also monitored and adjusted by means of their rotameters once per day). Overall, the flow rate uncertainty is considered to be a small contributor to the uncertainty of any measured species concentration.

Two integrating nephelometers (Meteorological Research Inc.) were present at the MHKC site. A Model 1593 unit ("unheated") was operated outside at close to the prevailing temperature, while a Model 1561 unit ("heated") was operated inside with an inlet heater that subjected the sampled aerosol to temperatures greater than 35 °C. The unheated unit was equipped with an inlet that allowed efficient sampling of particles as large as 15 μm, so that the nephelometer responsed both to coarse and to fine particles. Particular care was exercised in the calibration and operation of these instruments as described elsewhere (*10*).

Aerosol Sample Analysis. Analyses performed on the dichotomous sampler Teflon filters included mass measurement by β-attenuation, elemental analysis by XRF, absorption extinction (b_{ap}) by integrating plate light transmission, NH_4^+ by automated colorimetry, and SO_4^{2-} and NO_3^- by ion chromatography. The procedures and accuracies were similar to those summarized by Dzubay et al. (*18*), with the exception that measured values for b_{ap} were uniformly reduced by 35% to compensate for observed bias (*10*) in the integrating plate measurement method.

Nylon filter analyses for NO_3^- and SO_4^{2-} were performed by ultrasonic extraction in 10 mL, the extraction solution being the eluent (0.003 M $NaHCO_3$ + 0.0024 M Na_2CO_3) required in the subsequent ion chromatographic step. A wetting agent, BRIJ-35 (Technicon Product No. T21-0110, Tarrytown, NY 10591), was also added, in the amount of 5 μL L^{-1} of eluent.

Analysis for volatilizable carbon (C_{vol}) and elemental carbon (C_{el}) was performed on the quartz filters (0.35- or 0.089-cm^2 subsamples of the 6.2-cm^2 deposit area) by a two-step thermal method (630 °C in He, 850 °C in He/2% oxygen) described previously (*19*). Blank corrections were made with filters taken to the field and returned without use to the analytical laboratory. Measurements on 16 field blanks gave mean (standard deviation) values of 1.20 (0.08) and 0.069 (0.024) $\mu g\ cm^{-2}$, for C_{vol} and C_{el}, respectively. The mean blanks were 9% and 2% of the average loading for C_{vol} and C_{el}, respectively. From duplicate analysis performed on 23 of the ambient filters, the precisions of the C_{vol} and C_{el} determinations were estimated to be 5% and 13%, respectively.

Gas Measurements. Gas instruments at the MHKC were housed in a van whose air sampling system has been described previously (*18*). The van's interior was maintained near 20 °C. The instruments and their accuracies were Columbia Scientific Industries Model 1600 chemiluminescence NO_x monitor (larger of 5 ppb or 10%), Meloy Model SA700 pulsed fluorescence SO_2 analyzer (larger of 2 ppb or 10%), Bendix Model 1800 chemiluminescence O_3 analyzer (larger of 2 ppb or 10%), and Dasibi Model 3003 gas correlation CO monitor (larger of 200 ppb or 5%). The accuracy of each instrument was estimated from three multipoint calibrations performed over the course of the study, and zero level and span calibrations made at least on alternate days. Only zero and span calibrations were performed with the CO monitor, however.

The only gas measurement directly involved in the source apportionment calculations was that of NO_2, from which the extinction coefficient due to absorption by gases (b_{ag}) was calculated. The relationship (at 530 nm) is (*10*)

$$b_{ag}\ (Mm^{-1}) = 0.38[NO_2]\ (ppb) \qquad (1)$$

where the proportionality constant has been corrected for the average barometric pressure (840 mbar) and daytime temperature (2 °C) during the study.

Aerosol and Gas Concentrations

Averages. Table I gives diurnal averages of coarse and fine aerosol components, gas concentrations, and extinction components. The averages encompass about $^2/_3$ of the 20-day field study, based on those sampling periods for which valid measurements were simultaneously performed on *all* the components shown in the table, so that the magnitudes can be legitimately intercompared. Important features include (a) the dominance of carbonaceous material in the fine fraction, (b) major contributions to the fine fraction from nitrate, sulfate, and ammonium ions, (c) the larger concentration of coarse vs. fine mass, and (d) the larger concentrations of nighttime vs. daytime periods.

Sulfur–Sulfate. The separate day and night averages for the fine SO_4^{2-}/S ratio over the entire study period were 2.90 ± 0.14 and 2.82 ± 0.10, respectively (95% confidence limits). The theoretical value of 3.00 corresponding to all S being in the form of sulfate is within the confidence interval for the day ratio, and nearly so for the night ratio. In addition, the *t* test result for the difference in the averages, 0.08 ± 0.16, is consistent with zero at the 95% confidence level. The sulfur–sulfate comparison for the individual sampling periods is shown in Figure 1. Thus, our data do not confirm the "excess S" result found by Wolff et al. (*5*). In the coarse fraction, this relationship cannot be accurately tested because of light sulfate load-

Table I. Aerosol, Gas, and Extinction Component Averages Measured at Mile High Kennel Club in Denver from January 11–30, 1982[a,b]

	fine fraction			coarse fraction		
	day	night	uncertainty	day	night	uncertainty
mass, ng m^{-3}	18970	22490	2700	34810	36640	2700
C_{el}, ng m^{-3}	1840	2460	300			
C_{vol}, ng m^{-3}	5490	8730	800			
NO_3, ng m^{-3}	2570	1860	300			
NH_4, ng m^{-3}	1400[c]	1050[c]	200	33	−2	70
SO_4, ng m^{-3}	2280	1840	290	374	399	140
Al, ng m^{-3}	389	399	67	2720	3080	860
Si, ng m^{-3}	264	290	33	7060	7860	2300
P, ng m^{-3}	38	47	9	112	113	53
S, ng m^{-3}	755	662	52	250	272	160
Cl, ng m^{-3}	46	57	6	1400	1070	410
K, ng m^{-3}	59	98	4	634	662	43
Ca, ng m^{-3}	43	51	3	635	680	39
Ti, ng m^{-3}	5	6	9	88	92	13
Cr, ng m^{-3}	5	4	3	3	3	3
Mn, ng m^{-3}	8	13	2	20	21	3
Fe, ng m^{-3}	77	81	5	929	978	53
Ni, ng m^{-3}	3	3	1	4	6	1
Cu, ng m^{-3}	9	10	2	9	7	2
Zn, ng m^{-3}	38	54	3	38	39	3
Br, ng m^{-3}	78	128	4	21	27	2
Rb, ng m^{-3}	1	2	1	4	5	1
Sr, ng m^{-3}	1	1	1	9	9	1
Cd, ng m^{-3}	5	7	2	7	16	2
Ba, ng m^{-3}	29	33	14	59	56	25
Pb, nb m^{-3}	268	383	14	89	108	7
SO_2, ppb	7.4	7.5	2			
NO, ppb	30.4	57.3	5			
NO_2, ppb	25.6	31.6	5			
O_3, ppb	18.6	6.9	2			
CO, ppm	1.47	2.34	0.2			
b_{sp}, Mm^{-1}	79.0	110.8	4			
b_{sp} (35 °C), Mm^{-1}	55.1	77.4	3			
b_{sp}, Mm^{-1}	20.0	24.8	2			
b_{ap}, Mm^{-1}	9.7	12.0	2			

[a] Day is 0600–1800 MST; night is 1800–0600 MST. [b] Average concentrations of V, Co, As, Se, Sn, and Sb are less than 2 ng m^{-3}. [c] Includes assumed contribution from NH_4NO_3.

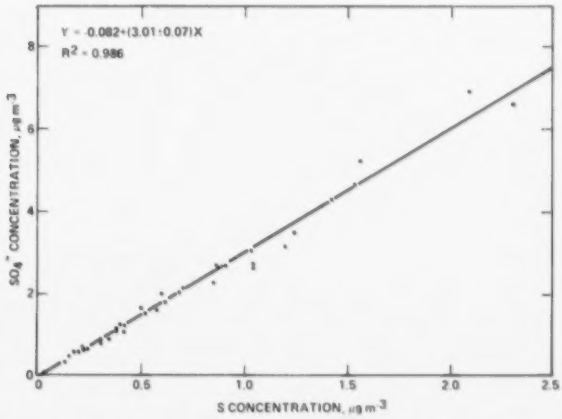

Figure 1. Plot of fine particle sulfate vs. fine particle sulfur.

ings and correspondingly poorer measurement accuracy.

SO_2–Sulfate. Because of the relatively isolated nature of the Denver airshed and the lack of a significant regional sulfate background in the western U.S., it is expected that sulfate in Denver originates primarily from the oxidation of local SO_2 emissions. For an ideal situation in which SO_2 is emitted from a single source and the SO_2 and resulting sulfate are transported to the measurement site along the same path, we have the relationship (*20*)

$$S_p/S_g = [R/(R + D_g - D_p)][\exp(R + D_g - D_p)t - 1] \quad (2)$$

Here S_p/S_g is the ratio of S in the particulate and gaseous form, R is the first-order reaction rate for $SO_2 \rightarrow SO_4^{2-}$, and D_g and D_p are the dry deposition rates for SO_2 and SO_4^{2-}, respectively. Using Table I to obtain the 24-h average $S_p/S_g = 0.070$ and taking $R = 0.003$ h^{-1} and $D_g - D_p = 0.007$ h^{-1} (obtained by reducing typical 24-h dry summertime values by a factor of 3), eq 2 can be solved to yield an aging time $t = 21 \pm 7$ h. The uncertainty corresponds to a simultaneous 25% decrease (50% increase) in R and $D_g - D_p$. Such a result even with its large uncertainty is consistent with the local origin hypothesis.

Nitrate–Nitric Acid. The fine particle nitrate averages given in Table I were obtained with the denuder difference sampler (DDS). Gaseous HNO_3 concentrations measured simultaneously in the procedure were found to average only 7% ± 14% of fine particle nitrate. Fine particle nitrate was also measured on the dichotomous sampler filters. The concentrations, however, averaged 7 times smaller than those found with the DDS, even though sulfate concentrations were in good agreement. Such a large difference between the two methods is a remarkable and important observation. Consistent with the experiments of Appel et al. (*21*), we speculate that the dominant cause of the "negative artifact" is evaporation of NH_4NO_3 from the filter due to the elevated temperature (35 °C) at which the interior of a Beckman dichotomous sampler is maintained. The assumption that NH_4^+ is the cation is speculative, since the nylon filters used in the DDS are unsuitable for NH_4^+ analysis. The assumption, however, is consistent with the finding of Wolff et al. (*5*). The

observation underlines the importance of using a DDS and the undesirability of heated dichotomous samplers for nitrate collection.

C_{vol}–C_{el}. As indicated above, the cut point of the sampler used to obtain the samples for carbon analysis was estimated to be 7 ± 2 μm, instead of the 2.5-μm cut point associated with all other fine elemental and chemical concentrations. Thus, the measured carbonaceous species presumably overestimated the true fine particle carbon values. Wolff et al. (*5*) found 70–80% of C_{vol} and C_{el} to occur in the fine fraction of winter Denver aerosol. A similar result was found by Zak et al. (*22*) in winter Albuquerque. Consequently, the carbonaceous values shown in Table I have been uniformly reduced by 15% in comparison with measured values to compensate for the cut point difference. The value of C_{vol} does not include multiplication by a factor of 1.2, which was used by Countess et al. (*1*) to account for the unmeasured hydrogen and oxygen in various organic compounds and thus referred to as "apparent organic carbon" rather than volatilizable carbon.

From Table I the ratio of elemental to fine particle carbon is similar for day and night, averaging 0.23. This contrasts with the substantially higher ratio of 0.46 found in the 1978 Denver Study (*1*). Since then, with a modified thermal procedure (*23*), the GMR group has consistently found smaller C_{el} percentages in subsequent field studies. Thus, the present result is credible and supports the view that the gross structure of carbonaceous aerosol in the winter Denver atmosphere is not qualitatively different from the pattern seen in most (urban or nonurban) ambient studies in the U.S.: C_{el} represents a small (but not negligible) fraction of the total carbon aerosol (*24*). Whatever residual uncertainty remains in the carbon results, it is important to emphasize that this has no effect on the source apportionment results presented later.

Extinction Components. The average values for b_{ap}, b_{sp}, and b_{sp} (35 °C) shown in Table I include multiplication correction factors of 0.65, 1.09, and 1.11, respectively. The first accounts for the previously mentioned bias in the integrating plate method, while the other two account for the angular truncation and sampling efficiency errors with integrating nephelometers (*25*). The resulting value of 0.24 for the b_{ap}/b_{sp} ratio is only about $^1/_2$ that reported in the 1978 study (*4*).

Soil Composition

To determine the soil contribution to the ambient aerosol and to distinguish soil- and woodsmoke-contributed K, a knowledge of the elemental composition of local soil was required. Bulk samples of street dust and exposed soil were collected at eight locations within several kilometers of the MHKC. In the laboratory each specimen was aerosolized and sampled by a dichotomous sampler to produce at least two filter pairs loaded with fine and coarse soil in the two size ranges identical with those of the ambient aerosol dichotomous samples. The aerosolization was performed with a TSI Model 3400 fluidized bed aerosol generator. The results of β-attenuation mass measurement and XRF analysis on the available 19 filter pairs are shown in Table II. The elements Cu and Sn were measured but not reported because of large contaminations from the bronze beads with which the specimens were mixed in the fluidized bed. The standard deviations mostly reflect true differences in the elemental compositions of the different specimens, since compositional results on filter samples from the same specimen always had a smaller standard deviation than the corresponding standard deviation indicated in the table. Nonetheless, there are several elements whose standard deviation is less than 15%, in both the fine and coarse fractions, and thus are potentially good soil tracers. Fortunately, the element relied upon in woodsmoke apportionment, K, also has a small variability in the soil samples. It will be noted that there is little difference in the elemental composition of the fine and coarse soil samples, beyond that due to specimen variability.

Table II. Denver Soil Composition (Eight-Site Average)

	fine, mg g^{-1}		coarse, mg g^{-1}	
	mean	SD	mean	SD
Al	70	±7	80	±10
Si	200	±30	280	±30
P	0.18	±0.8	0	±0.6
S	2.5	±3	1.3	±2
Cl	7.3	±20	9.5	±20
K	30	±7	32	±4
Ca	21	±20	18	±10
Ti	4.0	±0.9	5.5	±1
V	0	±0.2	0.18	±0.06
Cr	0.22	±0.2	0.29	±0.2
Mn	1.2	±0.6	1.1	±0.4
Fe	45	±7	44	±6
Ni	0.11	±0.1	0.11	±0.02
Zn	1.1	±0.8	1.1	±0.8
Br	0.021	±0.04	0.021	±0.01
Rb	0.17	±0.05	0.16	±0.02
Sr	0.28	±0.1	0.28	±0.06
Zr	0.34	±0.2	0.25	±0.08
Pb	0.75	±0.3	0.58	±0.3

Source Apportionment of Ambient Mass

Coarse Particle Mass Apportionment. Following the first step of the procedure of Kleinman et al. (*14*), a factor analysis was performed on the elements measured in the coarse ambient aerosol fraction. Only those elements were included whose measurement accuracy was at least 30% (see Table I). Factor analysis was performed with the BMDP software package (*26*), retaining all factors with eigenvalues ≥ 1 after Varimax rotation. The resulting five-factor solution, accounting for 97% of the system's variation, showed the following factor groupings: Ti, Si, Fe, Ca, K, Al, Rb, Sr, Mn; Br, Pb; Cl; Cu; Zn. The variables within each factor are listed in order of decreasing factor loading > 0.72. It was readily apparent that the eigenvalue criterion was effective in selecting the correct factor retention number, since the next potential factor contributed only $^1/_7$ of the variation of the previous one and contained no loadings larger than 0.2.

The first two factors are immediately identifiable from their composition as originating from soil and automotive exhaust. The last three factors are associated with only one prominent element each and are not so readily identified.

So many of the elements in the first factor have high loadings that there is considerable choice in selecting a tracer for this source. Iron was judged the best choice because it is the most accurately measured (Table I), it has one of the smallest variations in terms of its fraction of total soil mass (Table II), and it is a major component of soil. The obvious tracers for the remaining factors were Pb, Cl, Cu, and Zn. Taking these five elements as a candidate set of predictors for the measured coarse particle mass concentrations, a forward stepwise multiple linear regression was performed. Only Fe and Cl were found to be useful predictor variables, with the remaining variables having unphysical negative coefficients and large uncer-

Table III. Calculated Source Profiles[a]

	fine particles				coarse particles	
	soil	motor vehicle	woodsmoke	sulfate	soil	street salt
C_{el}, mg g^{-1}		200 ± 40 (240 ± 30)	67 ± 40 (86 ± 60)	33 ± 20 (0)		
C_{vol}, mg g^{-1}		650 ± 110 (720 ± 100)	390 ± 200 (570 ± 280)	150 ± 60 (0)		
NH_4, mg g^{-1}				130 ± 20 (160 ± 30)		
SO_4, mg g^{-1}				390 ± 50 (460 ± 70)		
Al, mg g^{-1}					86 ± 6	
Si, mg g^{-1}	200 ± 30 (200 ± 30)				260 ± 20	
S, mg g^{-1}				130 ± 20 (150 ± 24)		
Cl, mg g^{-1}						320 ± 80
K, mg g^{-1}	28 ± 4 (28 ± 4)		15 ± 4 (20 ± 8)		22 ± 1	
Ca, mg g^{-1}	44 ± 7 (47 ± 8)				22 ± 2	
Ti, mg g^{-1}					3.2 ± 0.2	
Mn, mg g^{-1}					0.63 ± 0.06	0.74 ± 0.3
Fe, mg g^{-1}	42 ± 10 (47 ± 13)	3.9 ± 0.9 (3.2 ± 0.9)			33 ± 2	
Br, mg g^{-1}		14 ± 2 (13 ± 2)				
Rb, mg g^{-1}					0.15 ± 0.01	
Sr, mg g^{-1}					0.23 ± 0.02	0.24 ± 0.1
Pb, mg g^{-1}		44 ± 6 (40 ± 5)				
CO, mg g^{-1}		290 000 ± 40 000 (280 000 ± 34 000)				
b_{sp}, m^2 g^{-1}		4.2 ± 0.9 (4.2 ± 0.9)	9.7 ± 2.5 (9.7 ± 4.6)	10.2 ± 1.7 (9.8 ± 1.9)		
b_{sp} (35 °C), m^2 g^{-1}		3.8 ± 0.7 (3.4 ± 0.5)	5.5 ± 1.5 (6.1 ± 2.7)	5.6 ± 1 (5.1 ± 0.9)		
b_{sp}, m^2 g^{-1}		2.9 ± 0.5 (3.1 ± 0.4)		0.40 ± 0.1 (0)		

[a] Values in parentheses result from substituting CO for Pb in the fine particle tracer element set.

tainties. This gave a regression equation for coarse mass M_c (34 cases, $R^2 = 0.96$):

$$M_c = 1870 + (30.3 \pm 1.5)[Fe] + (3.12 \pm 0.75)[Cl] \quad (3)$$

with ng m^{-3} as the units of M_c, [Fe], and [Cl]. The uncertainties (here and in all other regression equations in this article) are in terms of standard errors; 95% confidence limits are larger by about a factor of 2.

Coarse Particle Source Profiles. To aid in confirming (or establishing) the identify of the source with which each of the two tracers is associated, source profiles were mathematically generated by the regression–renormalization procedure described previously (*27*). This involves regressing the tracers against each element separately and then dividing each coefficient by the corresponding coefficient obtained from regressing the tracers against mass. The resulting profiles are shown in the last two columns in Table III. Profile values are given only for those elements that had a substantial multiple correlation (arbitrarily chosen as $R^2 > 0.8$) between the measured and regression-predicted values.

As expected, there is excellent agreement between the mathematically generated "coarse soil" profile of Table III and the measured "coarse soil" profile of Table II: the average difference over all elements is only 21%. The profile associated with Cl includes only trace amounts of Mn and Sr with rather large uncertainties. Using X-ray diffraction, Davis (*28*) found halite (NaCl) to consistute 6% of the mass of coarse particle ambient samples taken contemporaneously with those of the present study at the MHKC site and 26% of coarse particle sample mass from a nearby stockpile used for winter street sanding. A pure NaCl source profile would have a Cl content of 600 mg g^{-1}, to be compared with 320 ± 80 mg g^{-1} shown in Table III. Consequently, we identify the Cl-dominated source as "street salt", supporting a similar finding by Dzubay et al. (*29*) from a Denver sampling during January 1979.

Taking the product of each regression coefficient from eq 3 with the corresponding average concentration value of the associated tracer element results in the coarse mass apportionment shown in Table IV. The soil source is seen to account for 83% of the average coarse particle mass.

Table IV. Coarse Mass Apportionment at Denver MHKC during January 11–30, 1982

	μg m^{-3}	%
soil	28.3	83
street salt	3.8	11
other	1.9	6
total	34.0	100

Fine Particle Mass Apportionment. The availability of an accurate source profile for the fine soil component (Table II) provides an important starting point for source apportionment analysis of the fine ambient aerosol concentrations measured in this study. Combining the fine soil Si percentage from Table II with the measured amounts of fine ambient Si from Table I leads to the conclusion that airborne soil contributes less than 10% of the ambient fine particle mass. It is also apparent from a further comparison of these two tables that there must be a substantial nonsoil contribution to fine Al, Mn, and K, elements that one often associates with soil origins. In the hope of creating purer tracer variables, we chose to replace the measured elemental concentrations by "reduced" concentrations, in which the estimated fine soil contribution to that elemental concentration has been subtracted away. For example, [K] was replaced by

$$[K'] = [K] - (0.14 \pm 0.02)[Si] \quad (4)$$

where [K] and [Si] are fine ambient concentrations of potassium and silicon measured during the same sampling period. The coefficient of Si is the average value of the ratio K/Si for fine soil, computed from all the fine soil samples on which Table II is based. The uncertainty shown is the standard deviation, which is dominated by specimen variation rather than measurement accuracy. Assuming Si is a pure tracer for soil, the soil correction term is quite well-defined for potassium.

Applying factor analysis to the fine particle variables whose measurement accuracy was better than 25% resulted in the following factor groupings: Fe, Mn, Pb, Br; S, SO_4, NH_4; Ca, Si; K; Zn, Cl; Al; Cu; P. The variables within each factor are listed in order of decreasing factor

loading > 0.60, and the eight-factor solution accounts for 95% of the system's variation. The mathematical parameters of the factor analysis were identical with those previously given for the coarse particle factor analysis. Except for Si, all the variables are corrected for soil contribution through expressions similar to eq 4. The quantities C_{vol}, C_{el}, and $[NO_3^-]$ satisfied the above accuracy criterion but were not included in the factor analysis for two reasons: they are generally not very useful in tracing specific sources and, because of missing values, their inclusion would have reduced by 25% the number of cases available for the factor analysis.

The elemental composition of the first five factors suggests tentative identification of the underlying sources as motor vehicles, ammonium sulfate, soil, wood burning, and incinerator, respectively, with the origins of the remaining factors obscure. In truth, however, there is much that is dissatisfying about the fine particle factor analysis results: the amount of variance contributed by each factor decreases quite gradually, with no obvious indication of the proper number of factors that should be retained, in contrast to the coarse particle factor analysis; some of the variables are quite migratory, depending on the number of factors retained; a factor defined by a heavy loading of only one element can be a warning of erroneous data rather than representing an actual source. Thus, while the factor analysis conveyed some qualitative information about the interrelationships of the variables, its overall usefulness seems questionable in this case.

In contrast, the multiple linear regression of total fine mass produced simple results in a straightforward way. The candidate set of predictors was the same set of variables used in the factor analysis, each (except for Si) reduced by the estimated soil contribution. Both forward and backward stepwise multiple regression and the "all possible subsets regression" procedures showed that only reduced K, Pb, and S were useful predictors of fine mass (substituting Br for Pb or sulfate for S gave equally good fits). Of the three, the soil correction was significant only for K.

Two details of the mass regression should be noted. Although the regression did not identify Si as a significant predictor of fine mass, the ubiquity of soil aerosol argues in favor of including Si in the regression equation. This was accomplished by adding the term [Si]/0.20, taking the denominator from the measured fine soil profile of Table II. The reasonableness of this step was supported by a better regression result (smaller residuals and coefficient uncertainties) with the Si term than without. Secondly, the nitrate contribution was included by adding $[NO_3^-] \times (80/62)$ to both the measured fine mass and the predictor terms in the regression equation, where the numerical coefficient assumes that NH_4^+ is the associated cation. This approach was required by the fact that a negative artifact eliminated nitrate compounds from the measured fine mass, as noted earlier.

Equation 5 shows the best regression result obtained for fine particle mass M_f (36 cases, $R^2 = 0.90$):

$$M_f = 1080 + 1.29[NO_3^-] + 5.00[Si] + (22.7 \pm 2.9)[Pb] + (7.81 \pm 1.03)[S] + (68.4 \pm 19.3)[K'] \quad (5)$$

with ng m^{-3} as the units of all concentrations. As representations of the data, eq 3 and 5 have the same desirable attributes: (a) "missing source" intercepts, which are only about 5% of the average total mass; (b) regression coefficients with generally moderate uncertainties; (c) nearly normal distributions of residuals having no extreme outliers; (d) R^2 values ≥ 0.90.

Because the number of cases on which eq 5 is based is not large and because of its importance, the stability of eq 5 was examined with the jackknife procedure (*30*). In this procedure, the set of regression results obtained from separately deleting each case is combined to give new estimates of the regression coefficients and their standard errors that are nonparametric, i.e., not dependent on the normality assumptions that underlie classical regression. Using the formulas of ref 30, the jackknifed version of eq 5 is

$$M_f = (868 \pm 935) + 1.29[NO_3^-] + 5.00[Si] + (23.7 \pm 4.3)[Pb] + (7.92 \pm 0.92)[S] + (66.6 \pm 28.9)[K'] \quad (6)$$

The original and jackknifed equation are similar, except that generally larger standard errors occur in the latter. The comparison does support the conclusion that eq 5 is a reliable representation of the fine particle mass measurements.

A final variation on eq 5 examined whether or not CO could be considered equivalent to Pb as a tracer of fine particle motor vehicle emissions. Investigation of this possibility was motivated by the very high correlation ($R = 0.96$) of the CO and fine particle Pb measurements. The corresponding regression result (28 cases, $R^2 = 0.91$) is

$$M_f = 2530 + 1.29[NO_3^-] + 5.00[Si] + (3.56 \pm 0.43) \times [CO] + (6.67 \pm 1.05)[S] + (50.7 \pm 19.8)[K'] \quad (7)$$

with ng m^{-3} as the units of all concentrations, including CO. The smaller number of cases is a consequence of missing CO data. The quality of the fit (as indicated by R^2) is comparable with that of eq 5, and the agreement of the regression coefficients for corresponding [S] and K' terms is well within the standard error ranges. Finally, there is excellent agreement between the estimates for the average motor vehicle contribution (regression coefficient times average concentration of tracer), 7.24 ± 0.92 μg m^{-3} (eq 5) and 7.60 ± 0.92 μg m^{-3} (eq 7), using the same 28 cases. The demonstrated equivalence of Pb and CO in this study is a very important result for future consideration in view of the certain demise of Pb and Br as motor vehicle tracers, from the phaseout of leaded gasoline.

Fine Particle Source Profiles. Table III gives calculated profiles associated with the fine particle sources whose tracers are Si, Pb, S, and K′, obtained with a procedure analogous to the one used for coarse source profile generation. A comparison set of profiles is also shown (in parentheses) based on replacing Pb by CO. On average, the two sets differ by 19%. Once again, elements were subjected to the same $R^2 \geq 0.80$ criterion for inclusion in the profiles.

The calculated "fine soil" profile agrees well with the measured "fine soil" composition shown in Table II (the agreement for Si is, of course, perfect by definition). The difference for Ca is a factor of 2, but even this is within the limit allowed by the very high variability of the Ca composition of the soil samples.

The motor vehicle profile is consistent with expectations in that Pb and Br have a 3:1 ratio and most of the mass is carbonaceous. The crucial component of the profile is, of course, the Pb value, since the impact of the motor vehicle source is inversely proportional to it. The value 4.4% is one of the smallest ever reported, which motivated a careful consideration of its reasonableness. A monotonic decrease in Pb as a percentage of motor vehicle emissions in the U.S. is being driven by the decreasing Pb content of leaded gasoline, the decreasing use of leaded gasoline, and the increasing numbers of diesel engines (particularly

Table V. Lead Content of Gasoline and Motor Vehicle Fine Particle Source Profiles

site	sampling period	gasoline Pb, g gal^{-1}	source profile Pb, mg g^{-1}
Watertown, MA	June 1979–June 1981	1.8 (2.4–1.5)	72 ± 2[a]
Detroit, MI	July 1981	1.2	73 ± 53[b]
Denver, CO	Jan 1982	0.90	44 ± 6[c]
Albuquerque, NM	Jan–Feb 1983	0.85	43 ± 12[d]

[a] Thurston and Spengler (*15*). [b] Wolff and Korsog (*31*). [c] This study. [d] Zak et al. (22).

in heavy duty trucks). Table V is a compilation of the Pb content of fine motor vehicle source profiles as determined in recent receptor modeling studies. The gasoline Pb contents were taken from region-specific data (*32*). The table suggests that the Pb content of gasoline is the primary determinant of the Pb content of the motor vehicle profile, and that the Denver value from this study is generally consistent with other studies. Including CO in this "fine particle" profile is nontraditional but appropriate from the preceding discussion. The meaning of the entry is that each microgram per cubic meter of ambient fine particle mass from motor vehicle primary emissions is accompanied by 290 $\mu g\ m^{-3}$ (0.25 ppm) of ambient CO.

As expected, the wood burning profile is dominated by carbonaceous material. The key element, of course, is K, representing 1.5% of the woodsmoke emissions. Fine K directly measured in woodsmoke emissions (*33–36*) falls in the range 0.5–8%, exhibiting great variability. The measurement most directly comparable with the present one is from the 1983 Albuquerque study (22), since the woodsmoke component was extracted from ambient data in virtually the same way. The result was 0.50% ± 0.05%. Interestingly, the regression showed no significant contribution to CO from wood burning. While not unexpected, this is an important result in view of recent discussion that the traditional motor vehicle origin of CO may be challenged by wood burning in areas heavily impacted by the latter (*37*). This does not appear to be the case in Denver.

The chief characteristic of the "sulfate" profile is that $(NH_4)_2SO_4$ makes up $^1/_2$ of its mass. It is of a different character than the other three, since it arises from secondary transformation of SO_2 in the atmosphere, whereas the former three directly reflect the composition of primary emissions from the sources. Since the sulfate profile contains no characteristic tracers, additional information must be used to apportion its impact to the original SO_2 sources. The carbon components of the sulfate profile are noticeably different for the two tracer approaches, with the tracer set containing CO giving a null result.

Primary and Secondary Fine Mass Apportionment. Table VI gives the final step in the source apportionment of fine particle mass. The first column shows the daytime ambient impact of primary emissions from the three sources associated with the tracer elements Pb, Si, and reduced K, calculated from the product of the average daytime concentrations of each tracer element (Table I) and the corresponding regression coefficient from eq 5. The second and third columns show the daytime ambient impacts of those sources contributing to the sulfate- and nitrate-related atmospheric loadings. These contributions arise mainly from the atmospheric transformation of SO_2 and NO_x emissions and thus are secondary in nature. The column entries were calculated by assuming a direct proportionality to the SO_2 and NO_x emission rates for each source (see below), normalized so that the sulfate- and nitrate-related contributions separately sum to the total contribution inferred from eq 5. Column four gives the sum of primary and secondary contributions, and column five expresses each sum as a percentage of the total fine particle mass. The last two columns are analogous to the previous two, but for the nighttime results.

The emission rates for SO_2 and NO_x, on which the secondary contributions in Table VI were based, were taken from the Denver emissions inventory summary for Winter 1980 developed by Dennis (*38*). This appeared to be the most comprehensive and best documented seasonal inventory available in a time period sufficiently close to the time of our field study and corresponds to 111×10^3 and 223×10^3 Kg day^{-1} for the total SO_2 and NO_x emission rates, respectively. Dennis did not explicitly consider wood burning as a source of either SO_2 or NO_x. Setting these to zero in Table VI should be a good approximation, however, since wood contains little sulfur and wood combustion temperatures are too low to produce NO_x efficiently. These arguments can be developed more quantitatively from approximate estimates of wood burning emission factors for particulate, SO_2, and NO_x (*39*). In broad terms, the SO_2 emissions inventory implicit in Table VI is dominated by electric power generation (70%) mostly from coal combustion, while NO_x is dominated equally by motor vehicles (40%) and electric power (37%). These percentages are virtually the same as those used by Wolff et al. (*5*). Since the categories of Wolff's emissions inventories differ from those used by Dennis, a detailed comparison of the minor contributors was not pursued, other than noting their qualitative similarities.

The main features of the fine mass source apportionment are (a) the dominant contribution of motor vehicles, approaching $^1/_2$ of the total fine mass, (b) the significant contribution from electric power generation, and (c) the generally modest contribution from each of the remaining sources, although the wood burning impact doubles from

Table VI. Fine Mass Apportionment at Denver MHKC during January 11–30, 1982

	day (0600–1800 MST)[a]					night (1800–0600 MST),[b] total	
	primary	secondary		total			
	$\mu g\ m^{-3}$	sulfate, $\mu g\ m^{-3}$	nitrate, $\mu g\ m^{-3}$	$\mu g\ m^{-3}$	%	$\mu g\ m^{-3}$	%
motor vehicles	6.1	0.3	1.3	7.7	40	10.0	44
electric power generation	0	4.2	1.2	5.4	27	4.5	19
industry	0	0.7	0.5	1.2	6	1.0	4
refineries	0	0.7	0.1	0.8	4	0.6	3
space heating (nat gas)	0	0	0.3	0.3	2	0.2	1
space heating (wood)	1.5	0	0	1.5	8	3.9	17
soil	1.3	0	0	1.3	7	1.5	7
other	1.1	0	0	1.1	6	1.1	5
total	10.0	5.9	3.4	19.3	100	22.8	100

[a] 17 samples. [b] 19 samples.

Table VII. Fine Mass Apportionment during Day and Night Periods of Highest Mass Concentration

	Jan 18 (0600–1800 MST) (fine mass 47 $\mu g\ m^{-3}$), %	Jan 20 (1800–0600 MST) (fine mass 41 $\mu g\ m^{-3}$), %
motor vehicles	61	35
electric power generation	19	22
industry	4	5
refineries	2	3
space heating (nat gas)	1	1
space heating (wood)	7	28
soil	4	3
other	2	3
total	100	100

its daytime value to 17% at night.

It is important to appreciate that the contributions due to electric power generation, industry, refineries, and natural gas space heating are entirely determined by the relatively crude emissions inventory scaling method. This is due to the lack of suitable measured chemical species that would serve as tracers of the primary emissions from any of these sources. The good representation of fine mass (eq 5) without consideration of a primary mass contribution from any of these sources suggests that their individual primary contributions are probably modest. But the assumption that SO_2 and NO_x emissions from each of the source categories remain within the Denver airshed to the same extent, and thus generate local secondary products in proportion to their emission rates, was beyond verification in this study. Neutron activation analysis might have made possible the use of coal combustion tracers such as Se, at least to the extent of qualitatively confirming the dominant contribution of coal combustion—i.e., electric power generation—to the resulting sulfate.

Episodic Fine Mass Apportionment. The modest levels of air pollution during much of the field study call into question the relevance of the average percentage source contributions of Table VI to the highly polluted conditions that are associated with "Denver Brown Cloud" episodes. This question was examined by recalculating Table VI, employing the same regression coefficients and SO_2–NO_x inventory scaling, but using elemental and chemical concentrations from the day and night period having the highest fine mass concentration. Table VII shows the results in condensed form. Comparing Tables VI and VII suggests that motor vehicles will assume an even greater relative importance during daytime Brown Cloud episodes than their already important role as a contributor under less extreme conditions. The comparison also suggests a much enhanced contribution from woodsmoke during nighttime episodes, with its impact being comparable to that of motor vehicles and electric power generation.

Fine Mass Apportionment at Central Elevated Site. A regression analysis of fine particle data collected at the CFB site (100 m above street level) resulted in the equation for fine particle mass M_f (28 cases, $R^2 = 0.86$):

$$M_f = -791 + 5.00[\mathrm{Si}] + 68.4[\mathrm{K}'] + (20.5 \pm 3.2)[\mathrm{Pb}] + (4.24 \pm 0.64)[\mathrm{S}] \quad (8)$$

with all concentrations having units of ng m^{-3}. In comparison with eq 5 the NO_3^- term is absent because the Beckman sampler was ineffective in collecting particle nitrate and the supplementary nitrate sampler (DDS) used at the MHKC site was not available at this site. The regression procedure showed that the soil and woodsmoke tracers, Si and K′, were not significant predictors of fine particle mass. We chose to include them, however, by using the same coefficients as in eq 5. The coefficient for Pb in eq 8 is in good agreement with that found for eq 5 (omitting the [K′] term changes the Pb coefficient in eq 8 to 27.3 ± 3.2, degrading the agreement but still within the uncertainty limits). The coefficient for S in eq 8 is very close to what would be expected for pure ammonium sulfate (4.13) whereas the eq 5 result implies additional material (possibly H_2O) coexisting with the $(NH_4)_2SO_4$. We have no ready explanation for the difference. Using the average concentrations measured at the Cadillac Fairview site with the coefficients of eq 8, we find the following contributions to fine mass: motor vehicles (47%), electric power generation (22%), wood burning (17%), and soil (11%). These percentages do not include any nitrate contribution, whose principal effect would be to modestly decrease the latter two values. Comparing these values with those of Table VI, we see substantial agreement between the percentage contributions of each source to fine mass at the two sites.

Generalized Source Profiles

In addition to the usual elemental/chemical components of the fine source profiles (Table III), some nontraditional parameters also appear (CO and b_{ap} and b_{sp} for heated and unheated aerosol). Numerical values for the latter parameters were obtained by the same regression–renormalization procedure used with the elemental/chemical components. We refer to results such as those of Table III as "generalized" source profiles. The concept, of course, encompasses *any* characteristic that one has reason to expect is linearly proportional to ambient mass loading, but with a proportionality constant that depends on the source. It will be noted that the extinction parameters have particular units in contrast to the essentially dimensionless nature of all the other profile components. Thus, for example, the mobile source profile predicts a light absorption impact of $2.9 \times 10^{-6}\ m^{-1}$ for each microgram per cubic meter of ambient fine particle mass due to mobile source primary emissions.

As noted earlier, the inlet configuration of the unheated integrating nephelometer (b_{sp}) was designed to allow a high sampling efficiency for particles as large as 15 μm, i.e., encompasing both fine and coarse particle size ranges. Since the ambient coarse mass concentrations were even larger than the fine, it seemed prudent to allow for coarse mass tracers (coarse Fe and Cl), along with the fine particle tracers Pb, S, Si, and reduced K. In addition, fine particle nitrate was included as a candidate tracer, since it was expected to be a contributor to the nephelometer response even though it was drastically reduced in the dichotomous sampler measured mass, as discussed earlier. The regression, however, retained only fine Pb, S, and reduced K as significant predictors of b_{sp}. The rejection of the coarse tracers is unsurprising. For example, Lewis (*40*) has shown from Mie theory that coarse mass has an extinction impact of less than 10% that of an equal amount of fine mass. It has been suggested (*41*) that standard Mie theory may underestimate coarse particle impact by up to a factor 10, but the present result gives no support whatsoever to this controversial suggestion. Similarly, the rejection of fine Si is understandable, since the soil component that it presumably traces is a small fraction of the fine mass and, being the tail of a coarse mode, has a size distribution that is poorly matched to efficient light scattering. The rejection of fine nitrate is less understandable, since it appears to represent 10–20% of the fine mass. This may signal that the nitrate measurements are less accurate than Table I suggests. Finally, the b_{sp} regression result is less

Table VIII. Daytime Light Extinction Apportionment (530 nm)

	b_{sp}, Mm^{-1}	b_{sp}, Mm^{-1}	b_{ag}, Mm^{-1}	total, Mm^{-1}
motor vehicles	29	18	4	51
electric power generation	42	2	4	48
industry	7	0	1	8
refineries	7	0	0	7
space heating (nat gas)	0	0	1	1
space heating (wood)	15	0	0	15
soil	0	0	0	0
other	−21	0	0	−21
total	79	20	10	109

satisfactory than desired because of a substantial negative intercept (−14% of the average b_{sp}). The b_{sp} regression result for the heated nephelometer showed a similar percentage negative intercept.

The unheated b_{sp} regression result is striking, in the range of impacts that is predicted for the same amount of ambient mass loading associated with the three sources. The predicted high impact of the sulfate-related source is consistent with long-standing conjectures on sulfate as a high-efficiency light scatterer. We have no way, however, of judging the reasonableness of the motor vehicle and wood burning predictions, other than awaiting the verdict of subsequent experiments. The heated b_{sp} regression result predicts a less variable extinction impact, in the 4–5 $m^2\ g^{-1}$ range.

Extinction Apportionment

The extinction information in Table III and mass apportionment results in Table VI lead directly to the daytime extinction apportionment given in Table VIII. Each entry in columns one and two of Table VIII includes primary and/or secondary contributions from each source category to the indicated extinction component. For example, the top-left entry was computed from $4.2 \times 6.1 + 10.2 \times 0.3$. The third column expresses the NO_2 impact and was calculated by simply distributing the average daytime NO_2 light absorption coefficient (Table I) in proportion to the NO_x emission rate of each source, which by assumption is equivalent to the relative nitrate contribution given in Table VI. The "other" source entries are fixed by the condition that each column sum to the measured average daytime extinction component value shown in the bottom line. The units of the results are Mm^{-1} ($10^{-6}\ m^{-1}$). By accident, the "total" extinction coefficient is close to 100, so every entry in the table also can be regarded as an approximate percentage. Strictly, the "total" extinction coefficient should also include b_{ag}, the Rayleigh scattering coefficient of air, which would contribute about 10% more (12 Mm^{-1}) to the extinction indicated in Table VIII.

The least satisfactory aspect of Table VIII is the −21 Mm^{-1} unassigned contribution to b_{sp}. This is traceable mostly to the negative intercept resulting from the b_{sp} regression discussed earlier. This suggests at least a 20% uncertainty in the extinction impacts for the sources calculated in Table VIII.

Comparing Tables VI and VIII, it is apparent that the order of importance of the sources is essentially unchanged whether the basis is mass or extinction impact. The chief difference is the increased extinction impact of the electric power and wood burning sources, relative to their mass impact. The origin of the difference is the smaller unheated scattering coefficient per microgram per cubic meter from motor vehicles, compared with the wood burning and sulfate sources. If the scattering coefficient had been similar for the three sources, then the motor vehicle source would have accounted for the great majority of the total extinction, since it includes almost all the absorption effect in any case.

Table IX. Comparison of Fine Particle Mass Apportionments in Denver (24-h Average)

	Jan 1979,[a,d] %	Nov–Dec 1978,[b,e] %	Jan 1982,[c,e] %
motor vehicles	28	26	42
coal combustion (mainly electric power generation)	14	20	23
wood combustion	*f*	12	12
soil/flyash	3	12	6

[a] CMB: Dzubay et al. (29). [b] Emissions inventory assisted CMB: Wolff et al. (5). [c] Multiple linear regression: this study. [d] National Asthma Center. [e] Mile High Kennel Club. [f] Undetermined.

Comparison with Previous Denver Receptor Modeling

The present study is the third major receptor modeling attempt to arrive at a source apportionment of the Denver winter aerosol. After this much effort, it is not unreasonable to expect that a consistent picture should be emerging, if receptor modeling deserves to be taken seriously as a source apportionment approach. Table IX compares the percentages of fine particle mass contributed by the three dominant sources determined from the three studies (the 1979 study results were modified by the same SO_2–NO_x emissions inventory scaling procedures used in the other two studies, to make the three studies as comparable as possible). The "soil/flyash" source is also included because its contribution is one of the easiest to determine by receptor modeling (and one of the most difficult in dispersion modeling). The comparison is particularly interesting since three different receptor models are represented: conventional CMB, emissions inventory assisted CMB, and multiple linear regression. Because the agreement is so good for the (dominant) motor vehicle contribution found in the two earlier studies, it is tempting to conclude that 3 years later there has been a real increase in the percentage contribution from this source category. Such a conclusion is insupportable, however, because it does not take account of the uncertainty inherent in these estimates. For example, the 1979 CMB estimate is almost entirely determined by the Pb and Br components in the motor vehicle source profile, and reasonable alternatives to those actually chosen could have increased the apparent motor vehicle contribution by 25% or more (*42*). The more sound conclusion that can be drawn from the comparison is that all three studies show motor vehicles as the dominant (but not overwhelming) source and the others in the same descending order of importance.

Conclusions

(1) At the MHKC site motor vehicles were the largest contributors to average fine particle mass (42%) and daytime extinction (47%). Electric power generation was next largest, at 23% and 44%, respectively.

(2) During periods of highest fine mass concentration, the motor vehicle daytime contribution increased to 61%, while the nighttime contributions were more evenly distributed between motor vehicles (35%), woodsmoke (28%), and electric power generation (22%).

(3) The average contributions to (non-Rayleigh) daytime extinction at 530 nm were b_{sp} (73%), b_{ap} (18%), and b_{ag} (9%).

(4) Elemental carbon averaged 23% of fine particle carbon, which in turn was the largest component (45%) of the average fine particle mass.

(5) All fine particle sulfur was in the form of SO_4^{2-}.

(6) Although fine particle nitrate appears to have been measured correctly with the DDS, only 15% of that sampled with a dichotomous sampler was retained on the Teflon collection filter. We attribute the loss to ammonium nitrate evaporation induced by the elevated temperature (35 °C) at which the sampler's interior was maintained.

(7) Carbon monoxide was equivalent to fine particle Pb as a tracer of primary motor vehicle emissions.

(8) Percentage source contributions to fine mass at a central 100 m high site were similar to those at the MHKC site.

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Registry No. NH_4, 14798-03-9; SO_2, 7446-09-5; NO, 10102-43-9; NO_2, 10102-44-0; O_3, 10028-15-6; CO, 630-08-0; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl_2, 7782-50-5; K, 7440-09-7; Ca, 7440-70-2; Ti, 7440-32-6; Cr, 7440-47-3; Mn, 7439-96-5; Fe, 7439-89-6; Ni, 7440-02-0; Cu, 7440-50-8; Zn, 7440-66-6; Br_2, 7726-95-6; Rb, 7440-17-7; Sr, 7440-24-6; Cd, 7440-43-9; Ba, 7440-39-3; Pb, 7439-92-1; C, 7440-44-0.

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